

FERROELECTRIC THIN FILMS: PREPARATION OF A COMPLEX ALKOXIDE $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ THIN FILM

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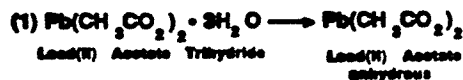
ABSTRACT

Ferroelectric thin films were prepared by sol-gel processing. The complex alkoxide was prepared by reacting a Lead (II) salt with Titanium and Zirconium alkoxides in a Methoxyethanol solvent. The gel was produced using a dilute acid catalysis to hydrolyse the bonds of the complex. The metal alkoxides were Ti/Zr isopropoxides, and Lead salt was a Lead Acetate. Working devices were not fabricated due problems in adhesion, cracking and problems with the viscosity of the gel.

INTRODUCTION

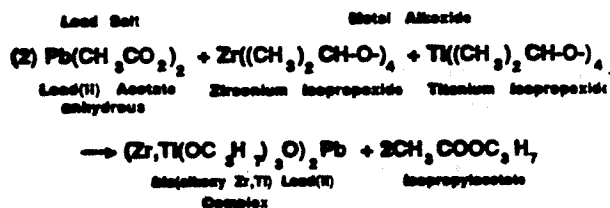
Ferroelectronic devices provide a promising new technology for memory design. This new surge in memory technology uses the ferroelectric effect of a Lead Zirconate Titanate thin film. The resultant Ferroelectric Random Access Memory (or FRAM, as trademarked by Ramtron Corp.) has the advantages of all present memory components. It has device densities greater than or equal to DRAMs; nonvolatility greater than EEPROMs; and the speed, life cycle endurance, and symmetrical read/write capabilities of SRAMs. It is as easy to use as SRAMs, and also has excellent radiation hardness [1,2].

The Lead Zirconate Titanate (PZT) thin film is used as the dielectric material for a memory capacitor. The PZT capacitor can be used in the same fashion as DRAM storage capacitors without the associated leakage. The PZT capacitor can also be used as a storage capacitor for SRAMs giving them memory retention. The difference between standard oxide capacitors and the PZT capacitor is that the PZT capacitor has two stable polarization states. This gives it the ability to be polarized in one direction and remain polarized in that direction until repolarized. The change of polarization state is accomplished by applying an electric field across the PZT thin film. Once the polarization state is set, the memory capacitor will hold that state until reset with a memory retention of greater than 10 years. The endurance of the device is greater than 10^6 R/W cycles [1,2]. This project is centered on the area of preparing the complex alkoxide PZT film. The complex gel was made by first dehydrating the Lead(II) Acetate trihydrate as in equation 1.



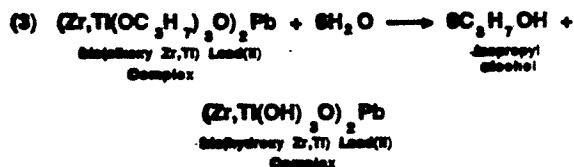
Equation 1

Next a Lead salt (Lead acetate) was reacted with Titanium and Zirconium alkoxide (Ti/Zr isopropoxide) as in equation 2.



Equation 2

The reactions were done using a solvent of 2-Methoxyethanol to dilute the complex and drive off impurities. A gel was then produced by diluting the bis(alkoxy Zirconato, Titanato) Lead(II) complex in 2-methoxyethanol and using water to hydrolyze the bonds of the complex as in equation 3.



Equation 3

The resultant gel is then coated on a wafer and the solvents are driven off on a hot plate. The perovskite phases crystallize from the bulk gels at temperatures between 450 to 600 degree Celsius [3]. The desired film is a 0.1 to 1.0 um Lead Zirconate Titanate compound (1:1 Zr to Ti ratio in the PZT). This should produce a ferroelectric thin film with a dielectric constant of approx. 750, remanent polarization of 20 uC/cm**2 and a coercive field of 20 kV/cm [4]. Most of the present research is done using the PZT thin film as a capacitor dielectric, this project was to evaluate the PZT thin film for use as a gate material for a Metal Ferroelectric Semiconductor device.

EXPERIMENTATION

The method of gel preparation is a combination of the methods used by Budd, Dey and Payne [3,4] and Gurkovich and Blum [5]. 600ml of 2-Methoxyethanol was transferred into a single neck round bottom flask and mixed with 5 grams of Calcium Hydride in a Nitrogen ambient. The solvent was refluxed for 72 hrs as seen in figure 1. The refluxed methoxyethanol was distilled off and collected in a 250ml flask. The Methoxyethanol that was refluxed and distilled is used to distill and redilute the Lead Acetate, and is used to dilute the bis(alkoxy Zirconato, Titanato) Lead(II) complex. Anhydrous Methoxyethanol was distilled off as needed. 17.08g (0.045 moles) of Lead Acetate trihydrate was added to 15ml of anhydrous Methoxyethanol and a stirbar in a two neck 500ml round bottom flask in Nitrogen. One neck held a thermometer in contact with the solution, the other neck had a distillation head with a septum mounted vertical. Figure 2 shows the apparatus set up.

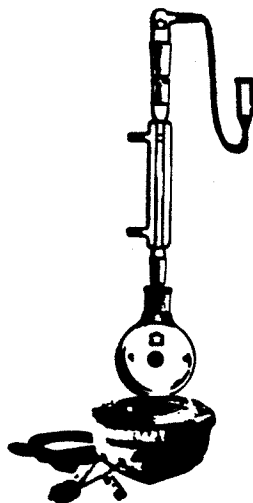


Figure 1:
Reflux Apparatus

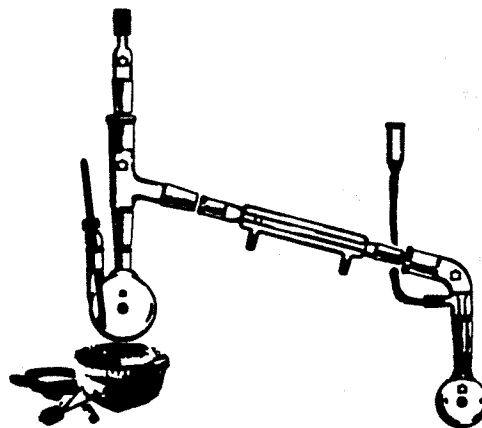


Figure 2:
Distillation/Reaction Apparatus

The solution was heated, at 118C the associated water was distilled off. Afterwards the temperature reached 124C, the boiling point of Methoxyethanol. Three successive distillation and redilutions were performed to remove the water from the salt. Titanium isopropoxide and Zirconium isopropoxide were transferred into syringes in a Nitrogen ambient. The distillation was stopped by cooling the solution when there was 15ml of Methoxyethanol in solution. The solution was cooled to 75C at which time 7.02ml (0.0225 moles) of Titanium isopropoxide and 6.20ml (0.0225 moles) of Zirconium isopropoxide were injected into the solution and mixed. The color of the solution changed from a golden to a light brown color. The temperature of the solution increased to 90C at which time the isopropylacetate was

driven off (B.P. 85 C) in the reaction. The temperature was increased to 150C to assure the reaction went to completion, then cooled to approximately 80C. Care must be taken when heating the solution because if overheated the complex will decompose. The solution was cooled to 65C and diluted with 60ml of anhydrous Methoxyethanol. 6.5ml of a 0.1 molar concentration of Nitric acid was added to the complex as the water of hydrolysis. The solution gelled rapidly and became too viscous to pour out of the reaction vessel. The gel was spooned out of the reaction flask and diluted in 100ml of anhydrous Methoxyethanol to reduce the viscosity however the gel never went back into solution.

Wafers were then evaporated with Al and sintered at 450C for 20 minutes. Attempts to spin coat the PZT complex on the wafers was unsuccessful due to the high viscosity. Ceramic thick films were evaporated with Chromium and the PZT gel was applied by means of screen printing and brushing it on. Due to the high viscosity and the poor adhesion to Chromium both methods were unsuccessful.

RESULTS & DISCUSSION

The results of this project is that the complex produced was similar to that obtained by Gurkovich and Blum [5]. This was demonstrated first, when the Lead Acetate trihydrate was dehydrated the associated water was driven off at 118C. Second, when the Ti and Zr isopropoxides were added to the Lead Acetate, the temperature rose as the reaction occurred, and the isopropylacetate was boiled off. Third, when the water of hydrolysis was added the solution gelled rapidly.

Ideas for future experimentation are that the complex should be diluted with more methoxyethanol than the 60ml used, I would try 120ml. Another idea is to use copper as the metal because it is necessary to be able to etch the thin film without etching the metal. An idea for an etchant would be a HF, HCl mixture.

Figure 3 shows the structure formed. This structure is a face-centered cubic with a Ti/Zr atom lying on a vertical axis.

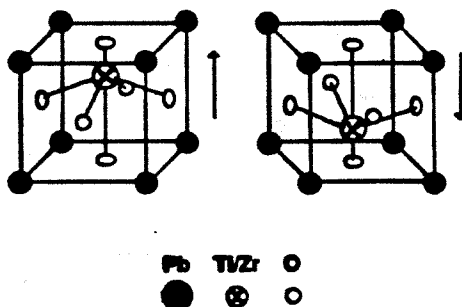


Figure 3: PZT Unit Cell

Titanium's electron configuration is similar to an Ar core with 2 electrons in the 3d and 2 electrons in the 4s levels. Zirconium's electron configuration is similar to an Kr core with 2 electrons in the 4d and 2 electrons in the 5s levels. The structure in figure 3 is formed when both Ti and Zr give up their electrons resulting in a positive four electron charge. The position of the Ti/Zr atoms is dependant upon the direction of the last field applied across the thin film. The thin film was proposed to be used in the following manners. First, the PZT thin film was to be used as a memory capacitor as shown in figure 4. Second, the PZT thin film was to be used as a gate material in different layer schemes as shown in figures 5,6,7. The Integrated Circuit design layout is located in the Appendix.

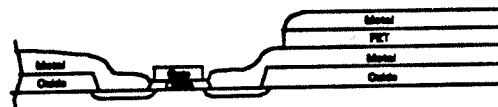


Figure 4 : PZT Capacitor



Figure 5 : Metal Ferroelectric Semiconductor Device



Figure 6 : Metal Ferroelectric Oxide Semiconductor Device

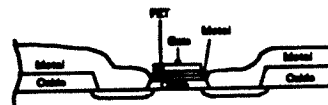


Figure 7 : Metal Ferroelectric Metal Oxide Semiconductor Device

SUMMARY

The crux of this lab was to prepare a PZT thin film capacitor using sol-gel processing to produce a liquid that could be spin coated on a Si wafer. The gel produced was too viscous to spin coat, the method of coating was to brush coat the PZT complex on the substrate. The resultant film had many cracks and could not be used as a dielectric. One possible reason for the cracks could be that when the complex was rediluted after the water of hydrolysis was added, the gel never went back into solution. Another reason could be that there was not enough Methoxyethanol used to dilute the bis(alkoxy Titanato/Zirconato)

Lead(II) complex.

ACKNOWLEDGEMENTS

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